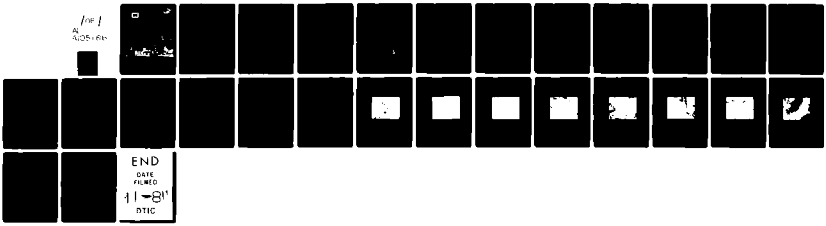
AD-A105 166 ARMY ENGINEER WATERWAYS EXPERIMENT STATION VICKSBURG MS F/G 13/2
BOREHOLE PLUGGING PROGRAM (WASTE DISPOSAL). REPORT 2. PETROGRAP--ETC(U)
SEP 81 J E RHODERICK, A D BUCK DE-AI97-81ET46633
UNCLASSIFIED WES-MP-C-78-1-2 NL



(9) Miscellaneous pp

LEVEL II

(14) WES-MP-18

MISCELLANEOUS PAPER C-78-1-21

AD A105166

(6) BOREHOLE PLUGGING PROGRAM (WASTE DISPOSAL).

Report 2.

PETROGRAPHIC EXAMINATION OF SEVERAL FOUR-YEAR-OLD LABORATORY DEVELOPED GROUT MIXTURES

by

(10) Jay E. Rhoderick, Alan D. Buck

(11) Sep 81

Structures Laboratory
U. S. Army Engineer Waterways Experiment Station
P. O. Box 631, Vicksburg, Miss. 39180

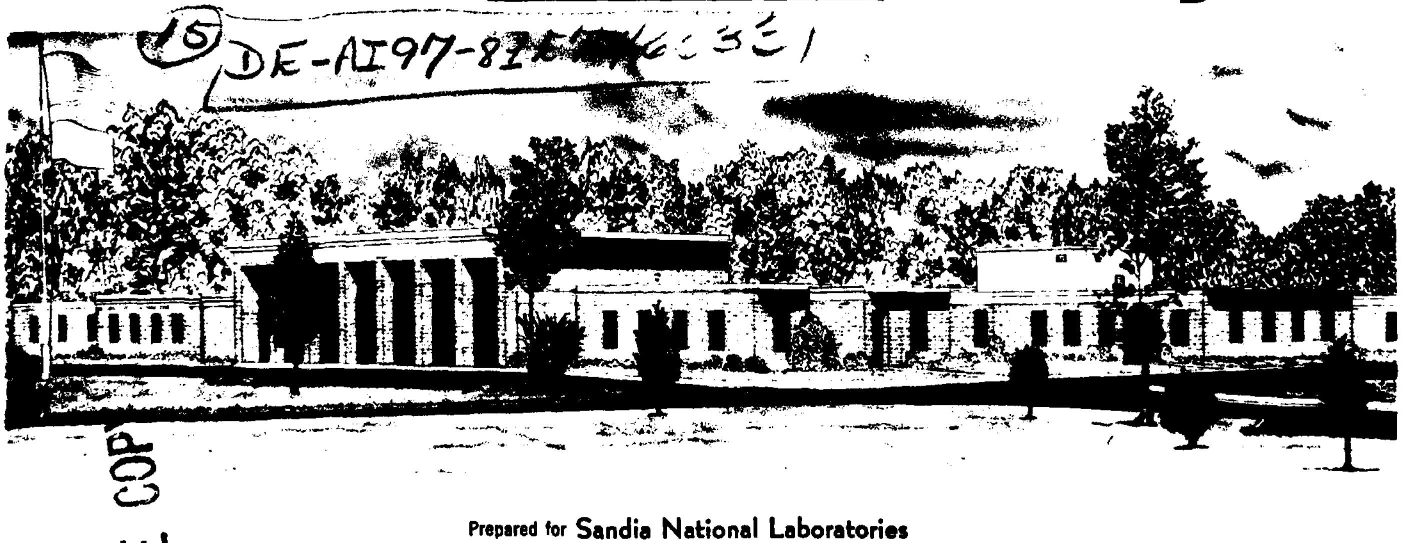
September 1981

Report 2 of a Series

(12) 24

Approved For Public Release; Distribution Unlimited

(15) DE-AI97-81



Prepared for Sandia National Laboratories
Albuquerque, N. Mex. 87115
and
Office of Nuclear Waste Isolation
Battelle Memorial Institute
Columbus, Ohio 43201

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Miscellaneous Paper C-78-1	2. GOVT ACCESSION NO. AD-A105	3. RECIPIENT'S CATALOG NUMBER 766
4. TITLE (and Subtitle) BOREHOLE PLUGGING PROGRAM (WASTE DISPOSAL); Report 2: Petrographic Examination of Several Four-Year-Old Laboratory Developed Grout Mixtures		5. TYPE OF REPORT & PERIOD COVERED Report 2 of a series 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Jay E. Rhoderick Alan D. Buck		8. CONTRACT OR GRANT NUMBER(s) U. S. Department of Energy Contract No. DE-AI97-81ET46633
9. PERFORMING ORGANIZATION NAME AND ADDRESS U. S. Army Engineer Waterways Experiment Station Structures Laboratory P. O. Box 631, Vicksburg, Miss. 39180		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Sandia National Laboratories Albuquerque, N. Mex. 87115 and Office of Nuclear Waste Isolation Battelle Memorial Institute, Columbus, Ohio 43201		12. REPORT DATE September 1981 13. NUMBER OF PAGES 21
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Available from National Technical Information Service, 5285 Port Royal Road, Springfield, Va. 22151.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Borehole plugging	Petrography
Cement grout	Scanning electron microscopy
Nuclear waste disposal	X-ray diffraction

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Specimens from five grout mixtures had been stored in either simulated brine groundwater at 73°F or in laboratory air for approximately 4 years. The variables included type of cement, use of a natural pozzolan, and use of salt in two mixtures. Available specimens were inspected; a specimen stored wet and one stored dry from each grout mixture were examined by X-ray diffraction for phase composition and by scanning electron microscopy to study microstructure.

(Continued)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT (Continued)

cont

The results showed that:

(a) Cracking of specimens was common; it was believed to be due mainly to temperature change and/or moisture change effects,

(b) The mixture variables were generally not recognizable, and

(c) The phase composition and microstructure of the five grout mixtures were considered normal.

PREFACE

This work was started for Sandia National Laboratories and completed for the Office of Nuclear Waste Isolation (ONWI), Battelle Memorial Institute, Columbus, Ohio. The latter work was performed under U. S. Department of Energy Contract No. DE-AI97-81ET46633, dated 5 November 1980. The work was done by the Concrete Technology Division (CTD) of the Structures Laboratory (SL), U. S. Army Engineer Waterways Experiment Station (WES). Storage and testing of the specimens will continue.

The investigation was performed under the direction of Messrs. Bryant Mather, Chief, SL, and John M. Scanlon, Jr., Chief, CTD. The samples and basic data were supplied by Messrs. Donald M. Walley and John A. Boa, Jr., of the Concrete and Grout Group. X-ray diffraction and scanning electron microscopy were done by Messrs. Jerry P. Burkes and Jay E. Rhoderick. This report was prepared by Messrs. Rhoderick and Alan D. Buck. Mr. Floyd L. Burns was the ONWI Project Manager. Mr. Boa was the Project Leader at WES.

Director of WES during publication of this report was COL T. C. Creel, CE. Technical Director was Mr. F. R. Brown.

CONTENTS

CONVERSION FACTORS, NON-SI TO METRIC (SI) UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to metric (SI) units as follows:

Multiply	By	To Obtain
angstroms	0.1	nanometres
Fahrenheit degrees	5/9	Celsius degrees or Kelvins*
inches	25.4	millimetres

* To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: $C = (5/9)(F - 32)$. To obtain Kelvin (K) readings, use: $K = (5/9)(F - 32) + 273.15$.

BOREHOLE PLUGGING PROGRAM

(WASTE DISPOSAL)

PETROGRAPHIC EXAMINATION OF SEVERAL FOUR-YEAR-OLD LABORATORY DEVELOPED GROUT MIXTURES

PART I: INTRODUCTION

1. Cement grouts have been under consideration as plugging materials in boreholes in and near nuclear waste repositories. The U. S. Army Engineer Waterways Experiment Station (WES), Structures Laboratory, Concrete and Grout Group, has developed grout mixtures for borehole plugging for Sandia National Laboratories. Five mixtures were cast in 1976 and 1977. Test specimens from these mixtures are approximately 4 years old and represent some of the oldest samples of grouts developed for borehole plugging of nuclear waste repositories. Specimens from these mixtures were tested and reported on in an earlier publication.* The five grout mixtures examined and their casting dates were:

- a. BPN-FA-BS-SP-P-1 (Type III) (22 February 1977).
- b. BPN-CS-FA-1 (15 December 1976).
- c. BP-521-25 MP (15 December 1976).
- d. BPN-FA-BS-SP-P-1 (16 August 1976).
- e. BPN-FA-SP-P (16 August 1976).

The most significant differences in the mixtures were as follows:

Mixture	Difference
BPN-FA-BS-SP-P-1 (Type III)	Contains Type III portland cement
BPN-CS-FA-1 BP-521-25 MP	Contain expansive cement in addition to shrinkage-compensating cement
BP-521-25 MP	Contains a natural pozzolan in addition to fly ash

(Continued)

* Boa, J. A., Jr. 1978. "Borehole Plugging Program (Waste Disposal); Initial Investigations and Preliminary Data," Miscellenous Paper C-78-1, Report 1, U. S. Army Engineer Waterways Experiment Station, Vicksburg, Miss.

Mixture	Difference
BPN-FA-BS-SP-P-1 BPN-FA-BS-SP-P-1 (Type III)	Contains fine salt

PART II: SAMPLES

2. Four samples, two wet and two dry, of each mixture were used for X-ray diffraction and scanning electron microscope (SEM) examinations. Samples were cured at 120°F* for 28 days after casting (Boa 1978). Samples were then divided into two groups for two testing environments. One group was kept inundated at 73°F in a specially prepared brine to simulate groundwater from a site near Carlsbad, N. Mex. These will be known as the wet samples. The other group was kept in a dry environment at 73°F. These will be known as the dry samples. In this case, dry means storage in laboratory air.

---

* A table of factors for converting non-SI units of measurement to metric (SI) units is presented on page 3.

PART III: TEST PROCEDURE

3. The samples were examined for surface cracks and flaws prior to preparation for X-ray diffraction and SEM examination.

4. Sample preparation for X-ray diffraction was determined by the amount and shape of the sample. The wet samples were taken from broken pieces of a 6-in. by 12-in. cylinder that had been cored. Each sample was prepared by sawing a 2-in. by 1-in. by 1/4-in. slab. Three mixtures (BPN-FA-SP-P, BPN-FA-BS-SP-P-1, and BPN-FA-BS-SP-P-1 (Type III)) had their samples cut parallel to the long axis of the cylinder. The other two mixtures had samples cut perpendicular to the long axis of the cylinder due to lack of enough sample in the longitudinal direction. The sawed surfaces were smoothed using methanol until saw marks were gone. Samples were kept in methanol and placed in a freezer when necessary to prevent additional hydration and carbonation. The dry samples were taken from smaller 2-in. by 4-in. cylinders. Attempts to saw a slab longitudinally in the cylinder failed as it would fracture. Consequently, an interior piece of each cylinder was ground to pass a 45-μm (No. 325) sieve.

5. X-ray patterns were made of slabs or powders with an X-ray diffractometer using nickel-filtered copper radiation. The sample was placed inside a vapor hood during this examination. The hood had an environment of static nitrogen gas and a wet sponge soaked with saturated barium hydroxide solution.

6. The SEM samples were dried in a vacuum at 50° C for up to 15-1/2 hr and then stored in a desiccator. At the time of examination, the sample was broken again for a fresh surface and to give a convenient sized piece to mount on a sample stub. The break was made so that the surface to be examined was from the same orientation as that of the X-ray diffraction sample. The sample was coated with carbon, then with an 80:20 mixture of gold and palladium. The total thickness of this coating was about 20 nm.

PART IV: RESULTS

7. Initial examination of specimens used for the X-ray diffraction samples showed cracking in all except that of mixture BPN-521-25 MP. However, additional examination of more specimens showed that cracking was present in some specimens of all five mixtures. This included specimens from wet and from dry storage. This examination was difficult for the wet specimens because deposits from the water tended to cover and mask the surfaces. Some of the specimens stored dry in plastic bags at about 73° F did not exhibit detectable cracks. Dry samples seemed to fracture more readily than wet ones. Some of the cracking that was seen is described in Table 1.

8. The X-ray diffraction patterns showed specimens from the five mixtures to be generally similar. Most contained ettringite, calcium silicate hydrate (CSH), calcium hydroxide (CH), quartz, and residual cement (7.3 Å). Other constitutents found in some of the samples were tetracalcium aluminate dichloride-10-hydrate ($C_3A(CaCl_2)H_{10}$),* tetracalcium aluminate monosulfate-12-hydrate ($C_4A\bar{S}H_{12}$), garnet-hydrogarnet solid solution series, sodium chloride (NaCl), calcite, and vaterite. The constitutents identified in each sample are listed in Table 2. All of the samples stored in the brine showed development of $C_3A(CaCl_2)H_{10}$ at the expense of ettringite, as would be expected; those mixtures made with salt (BPN-FA-BS-SP-P-1, BPN-FA-BS-SP-P-1 (Type III)) contained more $C_3A(CaCl_2)H_{10}$ than those not made with salt. In general, the other variables of presence or absence of expansive cement, presence or absence of a natural pozzolan, and presence or absence of portland cement were not detectable in the X-ray diffraction patterns. There was one indication of a recognizable difference due to a variable; mixture BPN-FA-BS-SP-P-1 made with expansive cement contained more $C_3A(CaCl_2)H_{10}$ than mixture BPN-FA-BS-SP-P-1 (Type III) made with Type III portland cement. This was true for both dry storage and storage in brine. Since both mixtures were made with salt, the ettringite had been wholly or largely

---

* Abbreviations where C = CaO, A = Al_2O_3, H = H_2O, $\bar{S}$ = SO_3.

converted to $C_3A(CaCl_2)H_{10}$. More $C_3A(CaCl_2)H_{10}$ in mixture BPN-FA-BS-SP-P-1 correlates with the use of expansive cement in it and more expansion (second column, Table 5 of Boa (1978)).

9. Approximately 17 scanning electron microscope micrographs were taken of each of the 10 samples for a total of 174 micrographs. Eight micrographs representing the five mixtures were selected for inclusion in this report. The samples showed typical hydration products for their constituents, age, and curing environments. A typical view of the grout at 2000X is shown in Figure 1. The dry and wet samples of each mixture appeared to be similar in their microstructure (Figures 2, 3, 4) with the dry samples occasionally looking weaker. The mixtures containing salt looked somewhat weaker than those without salt (Figure 4). Calcium silicate hydrate was visible in all of the samples (Figure 5). Figure 6 is a good example of massive calcium hydroxide in a mature paste. While ettringite was present in most of the mixtures by X-ray diffraction, it was not apparent in most of the 174 micrographs. None of these eight figures show recognizable ettringite. Figure 7 may show some crystals of $C_3A(CaCl_2)H_{10}$. Figure 8 shows a good example of a fly ash sphere that has been largely etched away leaving residual mullite and hydration product.

PART V: DISCUSSION

10. Sample ages ranged from about 3 years and 10 months to 4 years and 4 months when the examinations were made during December 1980. This range of about 6 months at these ages was not significant for the examinations that were made.

11. As mentioned before, the major variables in the mixtures were type or types of cements, type of pozzolan, and use of salt. However, since some specimens were stored in a simulated brine groundwater, the effect of the salt factor was largely eliminated for them. Wet or dry storage of specimens was a significant factor. The conversion of ettringite to $C_3A(CaCl_2)H_{10}$ in the presence of salt also largely eliminated the difference in amount of ettringite that might be expected when comparing non-portland and portland cement. The presence of a natural pozzolan in one of the five mixtures was not an especially significant factor and was not detectable in this work.

12. Specimens from each mixture were cured in two environments. One environment was storage in simulated brine groundwater at about 73^{o} F; the other was storage in laboratory air at about the same temperature. Some specimens from all five mixtures showed cracking. This cracking is believed to be due largely to the response of the high volume change of cement paste mixtures to changes in moisture or temperature. Changes in moisture content may have occurred when specimens were removed from storage in water for periodic testing or when the relative humidity of the laboratory air changed; temperature effects would include cooling after initial rise due to heat of hydration of the specimens, curing of at least some specimens for the first 28 days at 120^{o} F (Boa 1978, footnote to Table 3), and fluctuations in the laboratory temperature. Some cracking may also have been associated with differences in mixtures. The two mixtures made with salt (BPN-FA-BS-SP-P-1, BPN-FA-BS-SP-P-1 (Type III)) showed the most cracking.

PART VI: CONCLUSIONS

13. Five different grout mixtures that were approximately 4 years old were examined by X-ray diffraction and SEM. Variables between the mixtures included type of cement, presence or absence of a natural pozzolan, and presence of salt in two of the mixtures. Specimens from each mixture were stored dry at ambient laboratory temperature while companion specimens were stored in simulated brine groundwater, also at about 73° F. The following conclusions were made:

- a. Most of both wet and dry storage specimens showed cracking for all five mixtures. This was attributed to moisture or temperature changes or both in the laboratory environment.
- b. Specimens from all mixtures made with salt or stored in the simulated brine groundwater showed conversion of ettringite to $C_3A(CaCl_2)H_{10}$.
- c. The use of portland rather than shrinkage-compensating cement or shrinkage compensating plus expansive cement was not usually detectable, probably because of the ettringite conversion in the presence of salt.
- d. The use of a natural pozzolan in one grout mixture was not detectable.
- e. The phase composition and microstructure of the grout mixtures was normal for the materials involved, ages, and storage conditions.

BLANK PAGE

Table 1

Visual Examination of Specimens from

Five Grout Mixtures at About Four Years Age

Mixture	Type of Cracking
BPN-FA-BS-SP-P-1	
Wet	Hairline surface cracks, sample broken perpendicular to long axis*
Dry	Hairline surface cracks, specimen fractured along cracks when cut with saw
BPN-FA-SP-P	
Wet	Hairline surface cracks, sample broken perpendicular to long axis*
Dry	Hairline surface cracks, specimen fractured along cracks when cut with saw
BP-521-25 MP	
Wet	Some cracking was visible.
Dry	Some hairline surface cracks, specimen fractured when cut with saw
BPN-CS-FA-1	
Wet	Some hairline surface cracks, sample broken perpendicular to long axis*
Dry	Some hairline fractures, specimen fractured when cut with saw
BPN-FA-BS-SP-P-1 (Type III)	
Wet	Extensive cracks filled by white material, fractured when cut with saw
Dry	Extensive open cracks, fractured when cut with saw

* Breaks possibly due to laboratory handling.

Table 2

X-Ray Diffraction Data on Five Grout Mixtures at About Four Years Age

Mixture	Condition	Ettringite	Calcium Silicate Hydrate	$C_3A(CaCl_2)H_{10}$	$C_4A\bar{S}H_{12}$	Calcium Hydroxide	Residual Cement (7.3 Å)	Hydrogarnet††	Calcite	Quartz	NaCl*	Vaterite
		Constituent										
BPN-FA-SP-P												
	Wet	X	X	X	--	X	X	X	poss.	X	--	--
	Dry	X	X	--	X	X	X	X	poss.	X	--	--
BPN-FA-BS-SP-P-1												
	Wet	X**	X	X†	--	X	X	--	--	X	--	--
	Dry	X**	X	X†	--	X	X	--	--	X	X	--
BPN-CS-FA-1												
	Wet	X	X	X	--	X*	X	--	--	X	--	--
	Dry	X	X	--	X	X	X	--	--	X	--	--
BP-521-25 MP												
	Wet	X†	X†	X**	X†	X**	X	--	--	X	--	--
	Dry	X	X†	--	X	X	X	--	X	X	--	X
BPN-FA-BS-SP-P-1 (Type III)												
	Wet	X**	X	X†	--	X	X	--	poss.	X	--	--
	Dry	--	X	X†	--	X	X	--	poss.	X	X	--

* Salt is believed to be present in all the wet samples but was not detected by X-ray diffraction due to the type of sample preparation.
** These samples had the least amount of the compound that was detectable.
† The compound was most abundant in these samples.
†† Garnet-hydrogarnet solid solution series.

Figure 1. Micrograph 020281-20, X2000, mixture BPN-FA-BS-SP-P-1, dry sample. Fracture surface showing typical microstructure of the dry-cured grout mixtures. The bar is 10 μm long and the indication should read 10^{-5} m

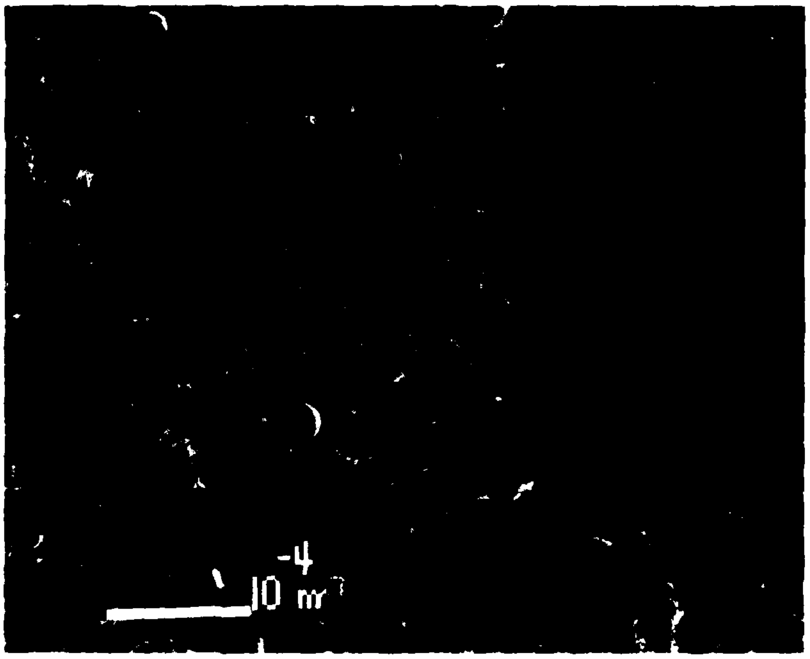


Figure 2. Micrograph 020281-7, X200, mixture BPN-FA-SP-P, dry sample. Fracture surface showing typical microstructure of the dry-cured samples of grout. The bar is 100 μm long

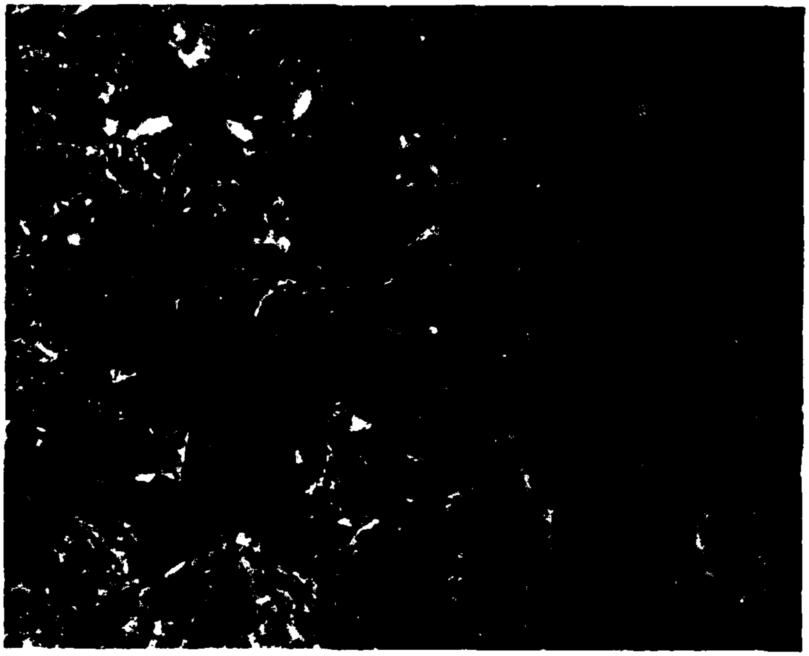


Figure 3. Micrograph 020281-7, X200, mixture BPN-FA-SP-P, wet sample. Fracture surface showing typical microstructure of the wet-cured samples of grout

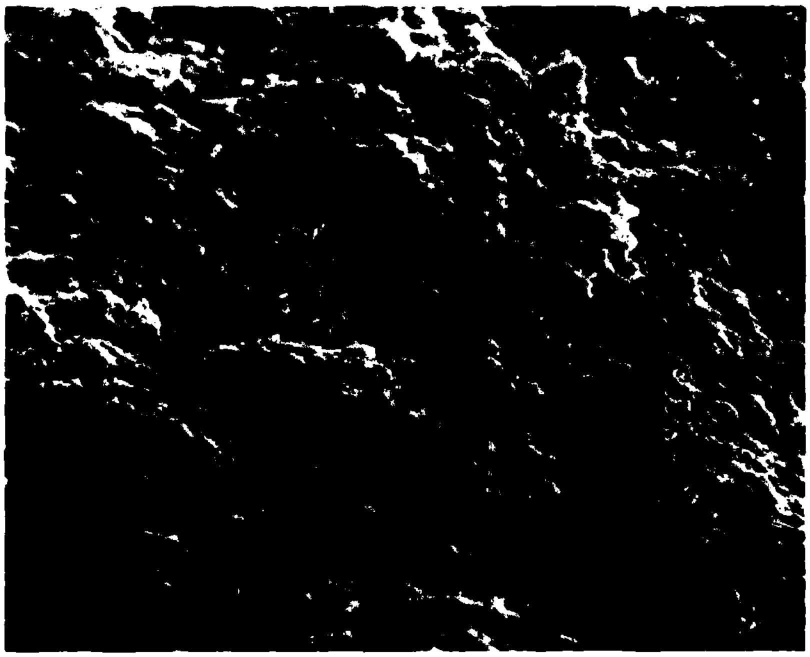


Figure 4. Micrograph 020381-19, X200, mixture BPN-FA-BS-SP-P-1 (Type III), dry sample. A fractured surface of a sample containing salt

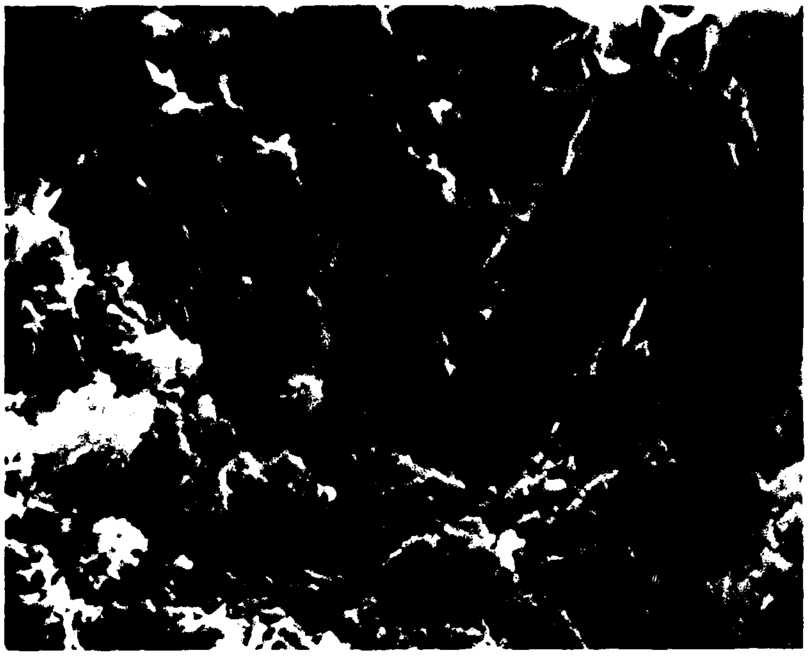


Figure 5. Micrograph 020681-55, X18,400, mixture BP-521-25 MP, wet sample. Fracture surface showing mostly reticular CSH

Figure 6. Micrograph 020681-21, X5000, mixture BPN-CS-FA-1, wet sample. Fracture surface showing massive calcium hydroxide crystals surrounded by CSH

Figure 7. Micrograph 021281-30, X4800, mixture BPN-FA-BS-SP-P-1, wet sample. Fracture surface showing calcium hydroxide and CSH; the platy crystals in the center may be $C_3A(CaCl_2)H_{10}$

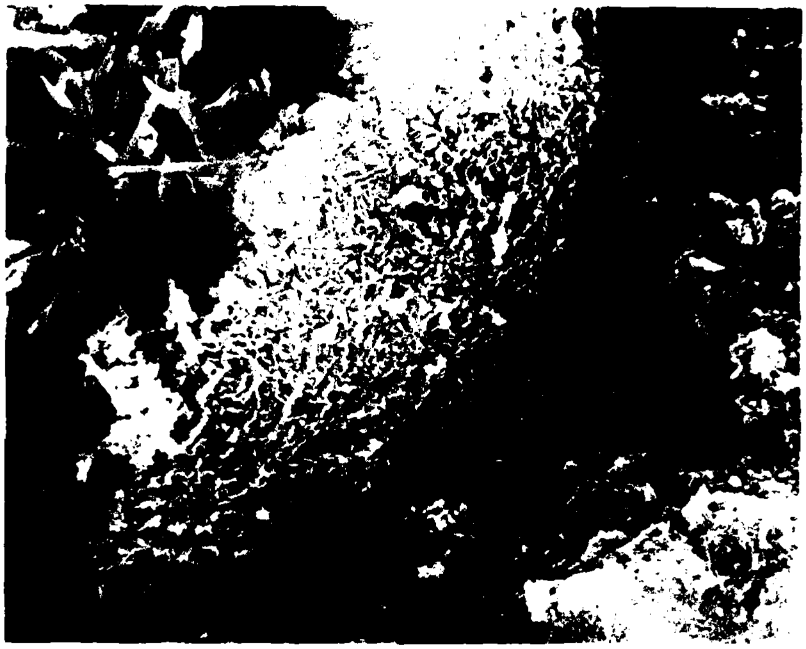


Figure 8. Micrograph 021281-15, X4800, mixture BPN-CS-FA-1, wet sample. Fracture surface showing part of an etched fly ash sphere. The crystals in the upper left corner are believed to be mullite originally present in this sphere

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

Rhoderick, Jay E.
  Borehole Plugging Program (Waste Disposal) : Report 2 : Petrographic examination of several four-year-old laboratory developed grout mixtures / by Jay E. Rhoderick, Alan D. Buck (Structures Laboratory, U.S. Army Engineer Waterways Experiment Station). -- Vicksburg, Miss. : The Station ; Springfield, Va. : available from NTIS, [1981].
  11, [10] p. : ill. ; 27 cm. -- (Miscellaneous paper / U.S. Army Engineer Waterways Experiment Station ; C-78-1, Report 2)
  Cover title.
  "September 1981."
  "Prepared for Sandia National Laboratories and Office of Nuclear Waste Isolation, Battelle Memorial Institute."

  1. Boring. 2. Electron microscopes. 3. Grout (Mortar). 4. Radioactive wastes. 5. X-rays--Diffraction. I. Buck, Alan D. II. Sandia National Laboratories.

Rhoderick, Jay E.
  Borehole Plugging Program (Waste Disposal) : ... 1981.
(Card 2)

III. Battelle Memorial Institute. Office of Nuclear Waste Isolation. IV. Borehole Plugging Program (Waste Disposal). V. U.S. Army Engineer Waterways Experiment Station. Structures Laboratory. V. Title VI. Series: Miscellaneous paper (U.S. Army Engineer Waterways Experiment Station) ; C-78-1, Report 2.
TA7.W34m no.C-78-1 Report 2

BLANK PAGE

LMED

8